SUMMARY REPORT

ARSENIC

Environment Canada
Conservation and Protection
Environmental Protection

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Canada

PACIFIC & YUKON REGION

ENVIRONMENT CANADA
CONSERVATION AND PROTECTION
ENVIRONMENTAL PROTECTION
PACIFIC AND YUKON REGION

CHEMICALS IN THE ENVIRONMENT
PACIFIC AND YUKON REGION

VI. ARSENIC

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1. INTRODUCTION

This report is one in a series entitled "Chemicals in the Environment - Pacific and Yukon Region" prepared by Environmental Protection. The objective of these reports is to provide the technical guidance necessary for: a) the interpretation of environmental quality data on specific chemicals, and b) the assessment of potential impacts resulting from the release of these chemicals into the environment.

The series will focus on both naturally occurring and man-made compounds which, when released to the environment, are of concern due to their persistence, toxicity and/or bioaccumulative abilities.

These reports discuss highlights of existing environmental quality data for B.C. and Yukon and provide information on environmental dynamics, potential impacts on the environment, and pertinent legislation and guidelines controlling both releases to the receiving environment and environmental quality.

2. USES AND SOURCES OF RELEASE

Arsenic occurs naturally in the earth's crust in association with copper, lead, silver or gold, usually as a sulfide. Major arsenic containing minerals are arsenopyrite (FeAsS), realgar (As_4S_4) and oripiment (As_2S_3) (1).

Arsenic (III) oxide is the most important commercial arsenic compound. It is emitted as a by-product during the smelting of copper and lead ores, and is recovered from the flue dust. Arsenic compounds have been used extensively in agriculture and forestry as pesticides, wood preservatives (usually in association with copper and/or chromium); glass, ceramic and cloth manufacturing; metallurgy; pharmaceuticals; and as livestock feed additives (2).

Arsenic compounds are released to the environment as a result of pesticide use, refining and smelting of nonferrous metals, fossil fuel combustion, incineration of municipal waste, the use of arsenic based wood preservatives and the burning of wood treated with arsenic based preservatives.

In past years, the major uses of arsenic coumpounds in Canada have been glass manufacture and metal rolling, casting and extruding (3).

Large quantities of arsenic compounds are used for wood preservation in B.C. The products CCA (chromated copper arsenate) and ACA (ammoniacal copper arsenate) are the major compounds used for wood preservation. These products are used for the treatment of fence posts, utility posts, construction and landscaping timbers (4,5).

The main source of environmental and groundwater contamination at wood treatment facilities is stormwater runoff from product storage areas. Due to the high toxicity of these compounds to aquatic organisms, the potential for serious environmental impacts as a result of major releases/spills is significant. However, there have been no such documented incidences in B.C. (4,5).

Valence changes of arsenic in the environment can affect its toxic potential. However, a preliminary study conducted in B.C. in 1986 for Environment Protection, indicated that soils and standing water collected in the yards at CCA facilities in B.C. contained at least 97% of the arsenic in the original pentavalent form (6).

Small quantities of the arsenical pesticide MSMA (Monosodium methane arsonate) are also used in B.C. for commercial thinning of conifer stands and for controlling mountain pine and spruce beetle by lethal injection into habitat trees.

3. ENVIRONMENTAL DYNAMICS

Arsenic is ubiquitous and exists naturally in the following oxidation states; elemental (As(0)), trivalent (As^{+3} and As^{-3}) and pentavalent (As^{+5}). In aquatic systems the presence of arsenic in the elemental form is rare. Arsenic can also occur in both organic and inorganic forms, with the chemical species dependent on the physical and chemical characteristics of the water system (7, 8, 9, 10).

In surface waters inorganic arsenate (+5) and arsenite (+3) forms predominate. Arsenate (AsO_4^{3-}) is the most chemically stable form under aerobic conditions, while low pH, anaerobic or reducing conditions favour the formation of arsenite (AsO_3^{3-}), arsines (As^{-3}), and arsenic sulfides (8, 11, 12). The oxidation of arsenic increases with salinity in marine systems (13). Fluctuations in trivalent/pentavalent arsenic ratios occur in some water systems and are probably associated with biological activity. The reducing actions of certain organisms can result in arsenite being the predominant form (10, 13, 14, 15).

Microbial reduction or biomethylation of arsenic occurs in freshwater and marine systems, but the rate depends on the species of organism and the environmental conditions (16, 17, 18, 19). Methanogenic bacteria and certain other organisms are responsible for the presence of low concentrations of dimethylarsinic acid (cacodylic acid) and methylarsonic acid in aquatic systems (20, 21). Dimethylarsinic acid is the major organic form of arsenic present in the environment. It is resistant to oxidation and may persist in natural waters. In anaerobic conditions further reduction of these compounds may result in the formation of volatile di- and trimethylarsines. As these compounds are released to aerobic environments at the sediment/water, water/air or soil/air interfaces they are probably oxidized to methylated compounds of higher oxidation state (8, 10, 14, 22, 23).

Dissolved arsenic in the water column can be coprecipitated with iron oxides or bound by suspended matter and humic constituents in the sediments. In waters with a high humic content, much of the arsenic is bound to colloidal humic material. Arsenite adsorbs and coprecipitates with other metal sulfides due to its strong affinity for sulphur. Arsenate adsorbs to

metal oxides and hydroxides. These processes prevent the buildup of high arsenic concentrations in surface waters (14, 22, 23, 25, 26).

Most of the arsenic in bottom sediments is present as hydrous iron oxides; sedimentary colloids; or chelated with humic material; while some is present in water soluble form. The release of arsenic from sediments is largely dependent on the reduction of the ferric ion (+3) to the ferrous ion (+2). Under anaerobic conditions, inorganic arsenic is leached from the bottom sediments in association with Fe. Arsenate binds more strongly to sediments than other arsenic forms (27, 28). Manganese oxides in the bottom sediments play an important role in the oxidation of arsenite to arsenate (29).

4. ENVIRONMENTAL LEVELS

4.1 Aquatic Systems

4.1.1 Freshwater

General

Arsenic concentrations in the water and sediments of lakes, rivers and streams vary substantially with proximity to industrial activity and ore deposits.

A survey of Canadian freshwater systems revealed that dissolved arsenic levels in rivers ranged from < 1 to 50 ug/L with 90% of the samples containing < 8 ug/L. Lake water samples contained < 0.5 to 20 ug/L (30). Occasionally, high arsenic levels have been detected in surface waters in the vicinity of arsenic-bearing mineral deposits, and in the hot springs. The major sources of aqueous contamination are nonferrous metal smelting and other industrial operations.

Most freshwater sediments contain natural arsenic levels of < 15 ug/g, but higher levels occur in the vicinity of naturally mineralized areas and in areas receiving arsenic contaminated industrial discharges.

TABLE 1 **ARSENIC LEVELS IN FRESHWATERS NEAR INDUSTRIAL ACTIVITY**

LOCATION	CONCENTRATION (mg/L)	REFERENCE
Near Au mining operations, Yellowknife	up to 12.6	30
Near arsenical pesticide manufacturer, Texas	up to 240.0	31
Downstream from industrial complex, North Carolina	up to 1.1	32
Near formulator of arsenical compounds, Union Lake, New Jersey	up to 2.8	33

TABLE 2 **ARSENIC LEVELS IN FRESHWATER SEDIMENTS IN AREAS OF NATURAL MINERALIZATION AND INDUSTRIAL CONTAMINATION**

LOCATION	CONCENTRATION (mg/kg dry weight)	REFERENCE
Au mining region, Yellowknife	up to 3500	34
Near firm manufacturing arsenical pesticides, Texas	100-12000	31
Mineralized area, Hackett River, Canadian Shield	up to 394	35
Red Lake, Canadian Shield		
- background	2-5	36
- near Au processing operations	up to 556	36
Near Cu smelter, Lake Washington, Washington	up to 210	37

4.1.2 Marine Systems.

General

Arsenic concentrations in seawater usually range from 0.15 to 6.0 ug/L and average 2 to 3 ug/L (8, 30). Elevated arsenic levels occur in

coastal waters in some areas receiving industrial discharges. Studies in the Puget Sound area in Washington State indicated that background levels of arsenic in water were 1.5 to 2.0 ug/L. However, samples collected near a copper smelter contained up to 1000 ug/L (9).

Natural arsenic concentrations ranging from < 0.4 to > 450 ug/g have been detected in ocean sediments, with average concentrations being approximately 30 ug/g (1). Elevated arsenic levels occur in sediments from some coastal and estuarine areas as a result of industrial releases. Sediments collected near the copper smelter in Puget Sound, Washington contained up to 10,000 ug As/g compared to background concentrations of 3 to 15 ug/g for this area (9). Similarly, concentrations of over 4000 ug/g have been detected in sediments from estuarine regions in southwestern England and were attributed to the extensive mining activity in that region (38, 39).

British Columbia and Yukon

Very little information was available on arsenic concentrations in B.C. freshwater systems. Arsenic levels in Fraser River surface waters were less than 5 ug/L at most sites sampled and did not exceed 10 ug/L (40). A limited number of water samples have also been collected from mining areas (41). In all cases, arsenic concentrations were well below the 50 ug/L guideline recommended by DOE for the protection of aquatic life and wildlife in freshwaters (3, 30).

Information on arsenic levels in sediments from freshwater systems in B.C. was also very limited. Low arsenic levels were present at all sites sampled in the Fraser River and its estuary (less than the detection limit of 8 ug/g dry weight in most cases) (41, 42). A limited number of sediment samples have been collected near mining operations and slightly elevated arsenic levels have been detected at some sites. However, these levels were typical for mineralized areas (41).

Information on marine waters off B.C. is almost non-existent. However, as a result of industrial releases, arsenic levels in sediments from several coastal areas of B.C. exceed background concentrations. Natural levels of arsenic in Burrard Inlet were found to be < 8 to 9 ug/g (41). However, much higher concentrations were detected in nearshore sediment samples taken immediately adjacent to certain industrial facilities.

Especially high concentrations were detected off an ore loading facility (up to 330 ug/g) and off certain shipbuilding/repair facilities (up to 483 ug/g). High arsenic concentrations were also found in Esquimalt Harbour sediments near the Department of National Defense docks (up to 180 ug/g) (41). Slightly elevated arsenic levels were also detected near other industrial sites such as False Creek, Alice Arm and certain coastal pulp mills (41, 43).

Several water bodies near mines and mining properties in Yukon have been monitored for arsenic. As would be expected in these highly mineralized areas, very high arsenic concentrations have been detected in the sediments (up to 842 ug/g) (44, 45). Surface water samples contained arsenic levels well below the DOE/L objective for the protection of aquatic life (50 ug/L) at all but one site (3, 30). Concentrations of up to 445 ug/L were detected in the South MacMillan area and were attributed to mining activity (46).

Creeks in the vicinity of Stokes Point on the Beaufort Sea contained < 0.5 ug As/L in the surface waters and 6 to 30 ug/g in the sediments (47).

Limited sampling has been done in the Beaufort Sea in the vicinity of Stokes and King Point. Seawater collected at Stokes Point contained 3 ug/L arsenic and sediments ranged from 5 to 182 ug/g. Sediments from King Point contained 10.1 to 20.2 ug/g (48).

4.1.3 Aquatic Organisms.

4.1.3.1 Uptake Arsenic uptake occurs in aquatic organisms under most environmental conditions, however, the rate of uptake is influenced by such factors as water temperature and the concentration and form of arsenic (49, 50).

Bioaccumulation of arsenic varies with the age and species of the organism, with the greatest accumulation occurring in species from the lower parts of the food chain. In most ecosystems studied there is no evidence of magnification up the food chain (22, 34, 51, 52).

Arsenic uptake in aquatic organisms occurs through the ingestion of contaminated food and suspended particulates, or by absorption through the skin and gills. The major route of uptake varies with the species (24, 53).

The primary sites of accumulation in aquatic organisms are the liver, spleen, kidney and digestive organs (53, 54). The kidney is thought to be important in arsenic metabolism and excretion (54).

In marine organisms, most of the arsenic is present in arseno-organic form. In several species including western rock lobster, dusky shark, whiting and several crab species, the predominant compound is arsenobetaine. It is believed that aquatic organisms can synthesize organic arsenic compounds from inorganic forms (55, 56, 57, 58, 59, 60, 61).

4.1.3.2 Levels

General

There is a wide variability in arsenic concentrations in the tissues of aquatic organisms, but the highest levels are normally found in species which live near the bottom sediments and ingest sediment particles while feeding. Arsenic does not biomagnify through the food chain and aquatic plants and crustaceans normally contain higher concentrations than most fish species (34, 60).

Most fish species show no correlation between arsenic levels in tissues and fish age, length or weight (50). However, in certain northern species (62, 63) and in Australian whiting (59) positive correlations have been observed. Similar correlations have also been observed in shrimp (64).

Liver, kidney and digestive organs normally contain higher arsenic levels than muscle tissue. However, high concentrations have been detected in muscle tissue in marine organisms and in freshwater species from contaminated areas (51, 54).

The average arsenic concentration in freshwater fish on a whole body basis is reported to be 0.54 ug/g (wet weight) (62). Freshwater fish collected across Canada contained 0.01 to 0.62 ug/g in edible tissue (30). Much higher concentrations have been detected near sources of industrial arsenic releases, especially gold mines (66).

Arsenic levels in marine species are usually much higher than in freshwater species. Some species of marine shellfish (especially crabs) and bottom feeding fish contain very high arsenic levels (> 100 ug/g dry weight) with no indications of abnormalities. These levels are normally attributed to natural enrichment rather than to industrial pollution (22, 65, 67).

The high levels of arsenic in seafood do not appear to pose a human health concern. The arseno-organic compounds have a short residence time when ingested by man and are excreted intact (61).

Marine plants, especially brown kelp, also contain very high levels of arsenic but concentrations vary widely with species. Submerged portions of the plants often contain higher levels than the emergent parts (53, 67). The average arsenic concentration in marine plants is approximately 30 ug/g (66). Most of the arsenic in plant tissues is present in water and lipid soluble arseno-organic forms (69).

British Columbia and Yukon

Arsenic levels in marine invertebrates from coastal areas of B.C. are high in comparison with other metals, but are similar to levels reported for invertebrate species from other areas of the world. In most cases, the presence of arsenic in B.C. marine invertebrates is attributed to the natural presence of arsenic in the environment and not industrial contamination.

Concentrations of 20 to 30 ug As/g (dry weight) were typical of crab muscle tissue from most B.C. coastal areas, although concentrations of over 100 ug/g were common in the mineralized and extensively mined Alice Arm area. Somewhat higher concentrations were often detected in the hepatopancreas (41, 42, 70, 71, 72).

Several species of shrimp from the southern coastal areas of B.C. contained mean arsenic levels in the 20 to 40 ug/g range. Arsenic levels in shrimp from certain other B.C. coastal areas were somewhat higher and mean concentrations between 60 and 80 ug/g were not uncommon. Levels of up to 300 ug/g were detected in the hepatopancreas (41, 70, 72, 73, 74).

In general, bivalves contained lower arsenic concentrations than crustaceans. Although the data for B.C. species are limited, mean concentrations appear to be in the 10 to 20 ug/g range. The exception is Yoldia collected from Quatsino Sound, which contained a mean concentration of 62 ug/g (41, 71, 72, 73).

Arsenic was also present in elevated concentrations in many species of B.C. marine fish and levels were comparable with those reported for fish from other areas of the world. Tissue concentrations in B.C. fish showed extreme variability and no clear trends were identified with respect to

species or geographic locations (41, 43, 70, 72, 73, 74). A wide variation in arsenic concentrations in marine fish has also been reported for areas other than B.C. and Yukon (75).

In general, B.C. data indicate that the highest concentrations were present in bottom-dwelling species such as sole and skate. Arsenic levels in the muscle tissue of sole were usually in the 40 to 80 ug/g range, although concentrations of over 100 ug/g were common in the Barkley Sound, Quatsino Sound and Surf Inlet areas (73). Skate contained arsenic levels of 77 to 182 ug/g in muscle tissue (73). Rockfish species generally contained lower arsenic concentrations (2 to 25 ug/g). A similar finding was reported by another author (75).

Although several researchers have reported that arsenic levels tend to be higher in the liver than in the muscle tissue of fish, this was not consistently observed for B.C. marine fish. In many instances, arsenic levels in muscle tissue exceeded those in the liver.

Very little information was available on arsenic levels in B.C. freshwater species. Tissue concentrations were typically much lower than in marine species, although slightly elevated levels have been detected in fish from mineralized areas (41). Arsenic was not detected in the muscle tissue of any of the several fish species collected from the Fraser River in 1973 and 1980. Arsenic was present in the liver of two fish collected in 1980 (76, 77).

No information was available for arsenic levels in aquatic biota from Yukon.

4.1.3.3 Toxicity A number of factors are important in determining the toxicity of arsenic compounds to aquatic organisms. These include the pH, DO concentration and temperature of the water; the chemical form and concentration of arsenic; the duration of the exposure; and the species and life stage of the exposed organism.

Sodium arsenite is generally considered to be more toxic to aquatic life than is sodium arsenate (8). Water systems with low pH and DO values favour the production of the more toxic lower oxidation states such as arsenite (11, 12). Warmer temperatures increase the rate at which aquatic organisms take up arsenic compounds and, therefore, in many species arsenic

has been shown to be more toxic in warm water conditions (49, 78). Studies with fish indicate that water hardness does not significantly affect the toxicity of arsenic (79).

Ambient water concentrations in the mg As/L range can result in adverse effects on the growth, reproduction and survival of aquatic organisms. Tests on the toxicity of sodium arsenite, to several species of freshwater fish, demonstrated that the 96 hr LC_{50} values ranged from 25.8 mg/L for brook trout to 72 mg/L for bluegill. The LC_{50} values for some species decreased with longer exposure times. A concentration of 18 mg/L was lethal to brook trout in an 11 day exposure and lethal to goldfish in a 14 day exposure (80).

In long term studies applications of sodium arsenite totaling 4 mg/L or greater (as $NaAsO_2$) caused decreased survival and growth in bluegill, with immature individuals being more sensitive than adults (51).

Concentrations of 1 mg/L arsenic trioxide resulted in loss of weight and fat content and also causes kidney damage in rainbow trout. This effect was manifested in the disruption of osmoregulatory mechanisms and water retention in the tissues (81).

In general, immature individuals are more sensitive to arsenic than are adults (49, 51). However, it was reported that the eyed stage of rainbow trout eggs were less sensitive to both arsenite and arsenate than both juvenile and adult fish. These eggs could tolerate a level of 50 mg/L, which was lethal to the swimming stages (82).

Trout embryos exposed to 0.1 to 0.75 mg/L arsenic (administered by injection into the yolk sac) had a 96% and a 46% hatch rate, respectively. In trout embryos surviving 1 mg/L and 0.25 mg/L exposures gross abnormalities were observed in 27% and 11% (83). The teratogenic potential of arsenic has also been observed in other studies (2).

Levels of 2 to 21 mg/L As^{203} were shown to be lethal to aquatic insects (2). When macroinvertebrates (including various insect larvae) in manmade ecosystems were exposed to arsenic concentrations of 4.0 mg/L over a treatment period of one year, a reduction in the survival and species diversity was observed. The effects on bottom fauna were proportional to the levels of arsenic in the sediments (51). Other invertebrate species exhibit a greater sensitivity to arsenic.

A concentration of 4 mg/L $NaAsO_2$ reduced zooplankton numbers by 5 to 10 fold, while a level of 8 mg/L resulted in immobilization and death (2). Daphnia exposed to 0.52 mg/L arsenic as Na_2HAsO_4 for a period of 3 weeks showed a 16% decrease in the survival rate. The LC_{50} value for this exposure period was 2.85 mg/L. A 50% decrease in reproduction was observed in Daphnia at 1.4 mg/l (84).

Additional information on the toxicity of arsenic to aquatic organisms is presented in Table 3.

4.2 Terrestrial Systems

4.2.1 Atmosphere

General

Natural sources of arsenic to the atmosphere include volcanic activity and natural weathering of the earth's crust. Major industrial releases occur during the processing of gold and base metal ores, fossil fuel combustion (especially coal), and iron and steel production. Solid waste incineration and pesticide application are less important sources.

TABLE 3: TOXICITY OF ARSENIC AND ARSENIC COMPOUNDS TO AQUATIC ORGANISMS

SPECIES	CHEMICAL FORM	EXPOSURE TIME	CONCENTRATION (mg/L)	EFFECT	REFERENCE
i) Aquatic Invertebrates					
Oyster - embryos	As_2O_3	48 hours	0.326	- 50% abnormal development	85
Oyster - embryos		48 hours	7.5	- LC_{50}	86
Mussel _ embryos	As_2O_3	48 hours	> 3.0	- 50% abnormal development	85
Mussels	$NaAsO_2$	--	4.3	- lethal	quoted in 2
Crab - zoeae	As_2O_3	96 hours	0.232	- LC_{50}	85
Crab	Total As	11 days	4.3	- toxic	87
ii) Fish					
Perch	total As	2 days	1.1	- toxic	87
Pike	total As	2 days	2.2	- toxic	87
Bleak	total As	3 days	2.2	- toxic	87
Bass	total As	10 days	7.6	- toxic	87
Carp	total As	4-6 days	3.1	- toxic	87
Goldfish	Arsenate	7 days	32.0	- LC_{50}	87
Goldfish	NA_3AsO_4	24-48 hrs	0.1-1.0	- behavioural impairment	86
Pink Salmon	total As	20 days	5.3	- 22% mortality	quoted in 2
Chum Salmon	total As	48 hrs.	11.0	- 50% mortality	quoted in 2

Arsenic in the atmosphere is present in both volatile form and in association with fine particulates (primarily as inorganic arsenic oxides and arsenate) (16). Dimethyl- and trimethyl- arsines have been detected in significant quantities in some locations (89). The highest arsenic concentrations are associated with the smallest particles (90). Atmospheric arsenic releases can be distributed over great distances by air currents, ultimately being deposited by precipitation and dry deposition.

Information on atmospheric levels of arsenic is limited. However, atmospheric arsenic levels in some remote areas are typically < 0.02 ug/m^3 (ranging from 0.005 to 0.1 ug/m^3) (91). Much higher levels are present in urban and industrialized regions, particularly in the vicinity of base metal smelters and gold processing operations. Precipitation samples collected in the Great Lakes area in the 1970's ranged from < 0.1 to 2.5 ug As/L. The highest levels were detected near highly industrialized sites such as Toronto, Sarnia, and Hamilton (92).

TABLE 4 ATMOSPHERIC ARSENIC CONCENTRATIONS

LOCATION	CHEMICAL FORM	CONCENTRATION (ug/m^3)	REFERENCE
Rural England	total As	0.0004-0.0064	91
Rural Canada	total As	0.0003-0.0047	91
Near a Au smelter, U.S.	total As	60-13000	2
Near a Au mine Yellowknife, N.W.T.	as AsO_2	0.01-3.91	93
U.S. cities	total As	0.01-1.41	94
- typical		0.02	94
Chicago	total As	0.02-0.04	2
Seattle	total As	0.03-0.14	2
New York	total As	0.02-0.05	2
British cities	total As	0.01-0.2	2

British Columbia and Yukon

Information on arsenic levels in the atmosphere of B.C. is very limited.

Atmospheric Environment Service recorded mean arsenic concentrations of < 0.10 to 0.40 ug/L in precipitation in south eastern B.C. between October, 1984 and February, 1986. Individual sample concentrations ranged as high as 3.1 ug/L. These levels are similar to those detected in

precipitation in Moncton, New Brunswick from June to November of 1981 (< 0.1 to 0.438 ug/L). It has been reported that mean arsenic levels in precipitation from various areas in North America range from 0.65 to 1.44 ug/L (95).

Dustfall in the vicinity of the Pb/Zn smelter in Trail in 1974 and 1975 ranged from 0.7 to 19 mg As/m^2.month (average of 4 mg/m^2.month), compared to a background level of 1 mg/m^2.month. A maximum concentration of 56 mg/m^2.month was recorded (96). In comparison, dustfall in the vicinity of a smelter in the Helena Valley, Montana ranged from 0 to 9.6 mg/m^2.month (97).

Dustfall collected in the Kimberley, B.C. area in 1974 and 1975 contained arsenic levels at less than the level of detection (3.5 mg/m^2·month) in all samples (98).

Arsenic concentrations in suspended atmospheric particulate matter in the Trail and Kimberley areas ranged from < 0.1 to > 0.5 ug/m^3 and from 0.01 to 0.20 ug/m^3, respectively (98).

No information was available on arsenic levels in the atmosphere and precipitation in Yukon.

4.2.2 Soil and Vegetation

General

Background arsenic levels in soils typically range from 0.1 to 40 ug/g (dry weight), with average concentrations of 5 to 6 ug/g (99). However, concentrations in soils vary significantly based on proximity to natural mineral deposits and soils over sulphide deposits can contain several hundred ug As/g.

Agricultural soils from Ontario contained from 1.1 to 16.7 ug/g arsenic and averaged 6.27 ug/g. These soils had no history of treatment with arsenical pesticides (100). Arsenic levels of up to several thousand ug/g have been detected in soils contaminated by arsenic releases from ore roasting and smelting, power plants and arsenical pesticide application (2).

The mobility or retention of arsenic in soils is influenced by both the level of contamination and the soil characteristics. Soils with a high clay or organic content retain arsenic, whereas sandy soils do not (101). Arsenic compounds in the soil are normally converted to arsenates (except

under reducing conditions) (11). Iron, aluminum, and in some instances phosphorus, bind the arsenate ion and restrict downward leaching in soil (102, 103). In contaminated areas, high arsenic levels are normally confined to the top 30 cm of soil (100, 101). However, soil pH affects the availability of Fe, Al and P and low pH values in soil can result in less arsenic retention and greater mobility (102). Anaerobic conditions can also result in the mobility of arsenic due to the formation of more soluble forms (104). The soluble inorganic forms of arsenic are more likely to leach from soils than organic arsenic compounds and instances of groundwater contamination have been reported (105).

The persistence of arsenic in soils is also influenced by its chemical form and the soil characteristics. Arsenic is removed from soils as a result of its reduction by microorganisms to volatile organic arsines. The rate of arsine production is greater under anaerobic conditions. Factors favouring microbial activity, such as warm temperatures and high organic content, increase the rate of decomposition (106).

Natural arsenic levels in terrestrial vegetation usually do not exceed 1 to 2 ug/g (dry weight) (2). However, vegetation in the vicinity of mines, smelters and other sources of arsenic, sometimes contains elevated arsenic levels (2).

The highest arsenic levels are normally found in the roots of plants with edible fruits and seeds containing relatively low levels, even in contaminated areas. Due to the toxicity of arsenic to vegetation, plants are usually killed or their development inhibited before significant levels can be accumulated by the edible portions. For this reason, the potential for reduced growth and productivity of vegetation and crops is usually of greater concern than its potential for accumulation (2, 104, 107).

Soil conditions which promote the mobility and solubility of arsenic in soils also increase the toxic potential of the soils to overlying vegetation. The toxic potential of soils is not accurately determined by measurements of total arsenic as not all of the arsenic is in soluble or available form. Measurements of extractable arsenic in soils are more relevant (52, 107).

British Columbia and Yukon

Information on arsenic levels in B.C. soils and vegetation was scarce.

Soil and water samples were collected at two B.C. facilities utilizing CCA (chromated copper arsenate) for wood preservation. High levels of arsenic, copper and chromium were detected in yard soils and in a ditch receiving surface runoff. Concentrations of up to 15,300 ug/g total As were present in ditch sediments. Levels of arsenic and also copper and chromium in surface runoff exceeded Canadian water quality criteria despite the fact that the facility sampled was taking precautions to avoid surface runoff contamination (6).

Emissions from a Pb/Zn smelter at Trail, B.C. release arsenic and other metals into the atmosphere. Analyses of vegetables grown in the Trail area in 1969 showed that arsenic concentrations were higher in root vegetables than green vegetables. In some instances, levels exceeded the 1969 Canadian Food and Drug guideline of 1 ug/g. However, it was noted that the highest concentrations were present in peelings of these vegetables and, therefore, probably would not be ingested by humans (96). No information was available on arsenic levels in soils from the Trail area.

Arsenic levels in soils from a Pb/Zn mine/mill complex near Kimberley were less than 16 ug/g, with the highest concentrations occurring near the acid plant. No information on vegetation from this area was available (98).

A study of arsenic levels in soils and vegetation was undertaken by EP near two abandoned mine sites in Yukon (108). The ores from this area contained high arsenic levels and concentrations of up to 19,000 mg/kg were present in soils (typical background levels were 30 to 300 mg/kg). Very high arsenic levels (up to 93.3 mg/kg arsenic dry weight) were detected in raspberries from areas receiving windblown dust accumulation. Higher levels were detected in the leaves (up to 2800 mg/kg in unwashed and up to 1600 mg/kg in washed). Much of the arsenic contamination on berries and leaves was attributed to dust. Surface washing reduced arsenic levels, although the residual high levels (up to 33.3 mg/kg in berries) indicate significant uptake into the plant. Raspberries are tolerant of high arsenic concentrations, thus allowing significant uptake into edible parts.

4.2.3 Wildlife

General

Very little information is available on arsenic levels in wildlife populations. Background levels in liver and kidney tissues of most species sampled are less than 0.3-0.5 ug/g (wet weight) (2, 91).

In most species, the highest arsenic levels are found in the liver, kidneys, spleen and lungs. Concentrations in the blood are very low with the exception of rats (2, 91, 109).

Positive linear correlations between liver and kidney arsenic concentrations have been identified in shorebirds from a contaminated area. Arsenic levels in liver were approximately twice those in kidneys (110).

Wading birds collected in a contaminated estuary in the Netherlands contained higher arsenic levels in tissues and feathers than did birds collected in comparatively uncontaminated areas. Arsenic levels in the kidneys of migrating birds increased rapidly after their arrival in the estuary. The mean arsenic concentration in kidneys of birds from this region was 6.6 ug/g compared to less than 3.5 ug/g in birds from Sweden (109). In another study in the Dutch estuary, levels of 4 to 15 ug/g (dry weight) were detected in the livers of shorebirds, while levels ranging from 2.5 to 10.5 ug/g were detected in the kidney. One bird found drowned in a net had an arsenic concentration of 100 ug/g in the liver. The authors speculated that the bird may have died as a result of locomotive impairment stemming from arsenic poisoning (110).

Shorebirds collected while wintering in industrialized bays in other locations contained 0.02 to 1.20 ug/g (wet weight) arsenic in the liver (average concentration of 0.10 ug/g) (111). Brown pelicans from the Gulf of California contained arsenic levels of 0.32 to 0.72 ug/g (dry weight) in the liver and 0.21 to 0.92 ug/g in the kidney (112). Arsenic levels in the liver, muscle and brain tissue of seven waterfowl species from New York State were less than the detection limit of 0.4 ug/g (113).

Waterfowl species which ingest lead shot were found to contain higher levels of arsenic in the feathers than birds that do not ingest shot (114). However, it has been shown that feathers do not respond proportionately to the level of arsenic exposure, and therefore should only be used as an indicator of arsenic exposure (114).

Small mammals collected from active and proposed minesites in Canada and the U.S. contained arsenic levels of less than 0.1 to 0.2 ug/g (wet weight) in most cases (115, 116). Background levels of arsenic in livers of rock squirrels and pack rats in Utah ranged from < 0.1 to 13.3 ug/g (dry weight). There was no correlation between the concentration of arsenic in the livers of these mammals and the levels in local soils and vegetation (117).

Arsenic was not detected (< 0.01 ug/g wet weight) in 21% of liver samples from white-tailed deer in Illinois. In samples with detectable levels, the mean concentration was 1.4 ug/g with a range of 0.6 to 4.8 ug/g (118).

Several tissues from Bowhead whales from the western Arctic have been collected and analyzed for arsenic. Arsenic was detected in the liver (0.024 to 0.085 ug/g wet weight), kidney (0.058 to 0.068 ug/g), and muscle (0.086 to 0.096 ug/g) but not in the blubber (< 0.002 ug/g) (119).

In contrast, arsenic levels in the blubber of narwhals from Northwest Territories were higher than levels in other tissues. Mean levels were; 12.1 ug/g wet weight in blubber, 0.162 ug/g in muscle, 0.343 ug/kg in kidney and 0.326 ug/g in liver (120).

British Columbia and Yukon

Information on arsenic levels in B.C. wildlife is very limited.

Arsenic concentrations were not detectable (< 7 ug/g dry weight) in liver, kidney and a few fat samples from various species of B.C. birds (mallard, Canada Goose, hawk, gull and widgeon). One liver sample from a mallard contained 10 ug As/g (121).

In 1986, samples of liver tissue were collected from deer from various areas of the province. Arsenic concentrations were less than the detection limit of 25 ug/g (dry weight) in all samples (122).

No information was available for wildlife species from Yukon.

4.2.3.1 Toxicity The toxicity of arsenic compounds to mammals and birds varies with the species of animal, the chemical formulation, the solubility of the compound, the route of exposure, and the rate of absorption, metabolism and excretion.

In general, the soluble arsenite form is considered to be more toxic than the less soluble arsenate. Inorganic forms are more toxic than organic forms and are less readily eliminated (2, 91). In general, arsenic compounds are eliminated more rapidly by small animals (2, 123). Elimination occurs mainly via the kidneys in all species (2, 17).

Unlike trivalent arsenicals (eg. arsenite), pentavalent forms (eg. arsenate) do not interfere directly with active enzyme sites. Arsenate can compete with inorganic phosphorus in phosphorylation reactions and has been shown to uncouple oxidative phosphorylation (91).

Arsenic trioxide administered with feed is more toxic than when administered in aqueous solution due to the low solubility of this compound (124). Inhalation of soluble arsenicals generally results in greater absorption than ingestion (2).

Wildlife species normally contain less than 0.5 ug/g arsenic (wet weight) in liver and kidney tissue. In animals dying of acute arsenic poisoning, these organs contain 2 to 100 ug/g arsenic. A concentration of more than 10 ug/g is considered to be indicative of arsenic poisoning. Concentrations are generally higher in the kidney than in the liver (2, 91).

Most species (except rats) excrete arsenic rapidly and in animals surviving toxic exposures, the arsenic concentrations in the liver and kidney may quickly decrease to levels not indicative of arsenic poisoning (2, 17, 125, 126).

Much of the information on toxicity of arsenicals to wildlife species was obtained during tests on arsenical pesticides or as a result of the misuse of these pesticides (91).

For most species the lethal oral dose is between 1 and 25 mg/kg body weight as sodium arsenite. The lethal oral dose for arsenic trioxide is 3 to 10 times higher (91). Luh et al. (87) estimate a general lethal dosage of approximately 44 mg As/kg body weight.

Studies on the toxicity of arsenic to game birds indicate that the order of sensitivity to arsenical pesticides is as follows; bobwhite > Japanese quail > ring-necked pheasant > mallard (91).

Pheasants and songbirds consuming large quantities of grasshoppers poisoned with arsenical insecticides, showed no toxic effects and very little arsenic accumulation (91, 127).

The misuse of arsenic acid as a pesticide in Tennessee resulted in mortalities in the local white-tail deer population. Pathological studies revealed that the deer died of massive hemorrhagic gastroenteritis. Mean concentrations in the liver, kidney and rumen contents of the deer were 18.96, 17.78, and 22.5 ug/g, respectively (128).

In the 1940s and 50s sodium arsenite was used to debark trees in various parts of the United States. Mortality among wildlife species including deer, porcupine and rabbit resulted. In New York State it was shown that 923 to 2770 mg of arsenic (as sodium arsenite) was lethal to deer when licked from the bark of trees (91, 129).

Contamination of ditch runoff water with MSMA (an arsenical pesticide) was thought to be the cause of a deer kill in Tennessee. High concentrations of arsenic were present in various tissues: 58.8 ug/g in the liver; 63.0 ug//g in the kidney; 25.2 ug/g in the muscle; and 332.0 ug/g in the rumen contents (91).

There have also been several incidents of arsenic poisoning in domestic animals resulting from the contamination of food and forage (91).

Arsenic affects tissues that are rich in oxidative systems such as; the alimentary tract, kidneys, liver, lungs and epidermis. It is a potent capillary poison (91). Studies with mice indicate that exposure to large doses of arsenic can result in decreased resistance to viral diseases (130). Teratogenic and mutagenic effects have also been observed in experimental animals, however, there is little evidence of carcinogenicity (2, 17, 91, 131). Inorganic arsenicals can cross the placental barrier in most mammals and, therefore, maternal exposure can result in fetal death or injury. Studies with organic arsenic compounds indicate that they concentrate in the placental tissue but do not cross it (2, 17, 91).

Symptoms of arsenic poisoning vary depending on whether exposure is acute or chronic exposure. They include abdominal pain, staggering gait, weakness, trembling, diarrhea, nausea, partial paralysis of the rear limbs, decreased growth, and degenerative effects on the kidney, liver and skin (2, 17, 91).

5. REGULATIONS AND GUIDELINES

Current regulations and guidelines pertaining to arsenic in the environment are summarized following.

5.1 Water Quality

The "Chemicals in the Environment" reports include environmental quality guidelines or criteria for these chemicals if such recommendations are available. Guidelines are provided for reference as one source of information in assessing environmental quality. It must be emphasized that guidelines must not be used in direct isolated comparisons with monitoring data. Site specific factors including local biophysical conditions must also be considered. For example, it must be recognized that guideline numbers may need to be modified to suit local aquatic conditions (eg. toxicity of ammonia varies with pH, toxicity of many chemicals varies with presence of other toxicants, toxicity of most chemicals varies with species and life stage affected). Likewise, guidelines or criteria information cannot be used directly in formulating water quality objectives but requires consideration of site specific biophysical and socio-economic factors and requirements (132).

At present Canada does not recommend water quality guidelines for acceptable concentrations of arsenic in marine waters. However, the U.S. Environmental Protection Agency Water Quality Criteria for arsenic state that "except possibly where a locally important species is very sensitive, saltwater aquatic organisms and their uses should not be affected unacceptably if the four day average concentration of arsenic (III) does not exceed 36 ug/l more than once every three years on the average and if the one-hour average concentration does not exceed 69 ug/l more than once every three years on the average." Toxicity information for other forms of arsenic was insufficient to establish guidelines (7).

The water quality guideline recommended by Water Quality Branch, Inland Waters and Lands Directorate for the protection of aquatic life in freshwater systems is 0.05 mg/l as total arsenic (30). The International Joint Commission recommended this value as the objective for total arsenic in the 1978 Canada/U.S. Great Lakes Water Quality Agreement. The Canadian

Water Quality Guidelines prepared in 1987 for the Council of Resource and Environment Ministers also recommended that concentrations of total arsenic in freshwater should not exceed 0.05 mg/L (3).

The U.S. Environmental Protection Agency Water Quality Criteria for arsenic states that "except where a locally important species is very sensitive, freshwater aquatic organisms and their uses should not be affected unacceptably if the four day average concentration of arsenic (III) does not exceed 190 ug/l more than once every three years on the average and if the one-hour average concentration does not exceed 360 ug/l more than once every three years on the average". Toxicity information for other forms of arsenic was insufficient to establish guidelines (7).

The EPA believes that measurements of acid soluble arsenic for water quality criteria would be more applicable than measurements of total arsenic and is considering the development of approved methods for acid soluble analyses. Until such methods are approved the EPA will apply criteria based on measurements of total arsenic (7).

5.2 Human Health

The Guidelines for Canadian Drinking Water Quality (133) and the British Columbia Drinking Water Quality Standards (134) recommend a maximum acceptable concentration of 0.05 mg/L total arsenic and an objective concentration of 0.005 mg/l.

Canadian Health and Welfare Food and Drug Regulations specify a tolerance level of 3.5 ug/g arsenic in fish protein (wet weight basis). Measurements of arsenic in extractable dried fish protein are not directly comparable to measurements in edible fish tissue. There are presently no guidelines on acceptable levels of arsenic in fish and shellfish for human consumption. Incidents of unusually elevated arsenic levels in commercially important species are reviewed on a case by case basis. However, studies have shown that the arsenic in seafood is predominantly in the form of arseno-organic complexes. These compounds are readily excreted and do not appear to pose a health hazard to consumers (61).

5.3 Ocean Disposal

The ocean disposal of wastes and other materials off the Canadian coast is controlled under the Federal Ocean Dumping Control Act. Arsenic is a 'restricted' compound under this Act. Although there are no set limits for the maximum level of arsenic in materials to be ocean disposed, applications for the disposal of materials containing arsenic are reviewed on a case by case basis.

Provincial criteria for the ocean or freshwater disposal of dredged material in Quebec stipulate a maximum concentration of 6 mg/kg arsenic.

5.4 Industrial Effluents and Emissions

Federal and provincial legislation provide controls on the entry of arsenic into the environment.

The level of arsenic in specific industrial effluents and atmospheric emissions is regulated under provisions contained in the British Columbia Waste Management Act, as well as general provisions and regulations issued pursuant to the federal Fisheries Act and the Clean Air Act.

The transport of arsenic compounds and arsenic-contaminated wastes is regulated under the Transportation of Dangerous Goods Act (Canada). Regulations under this Act came into effect on July 1, 1985 and are administered jointly by the Federal and various Provincial and Territorial governments.

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